### **NERL Research Abstract**

EPA's National Exposure Research Laboratory GPRA Goal 1 - Clean Air APM # 442

Significant Research Findings

# Recommended Methods for Ambient Air Monitoring of NO, NO<sub>2</sub>, NO<sub>Y</sub>, and Individual NO<sub>Z</sub> Species

#### Scientific Problem and Policy Issues

Monitoring instrumentation is needed to evaluate the effectiveness of nitrogen oxide  $(NO_x)$  emissions reduction as initially envisioned in the September 1998 final Regional Transport of Ozone Rule  $(NO_x \text{ SIP Call})$ . As part of this document, the Federal government proposed that 22 eastern states and the District of Columbia reduce source emissions of  $NO_x (NO + NO_2)$  in order to reduce downwind ozone concentrations. Although still being argued in the courts, some form of emissions reduction is likely to occur. Determining the effectiveness of these reductions on lowering downwind ozone levels will require accurate experimental measurements of ozone and ozone precursors, including the  $NO_x$  both before and then after full implementation of emission controls in May, 2004.

#### Research Approach

The objective of this report is to make recommendations on the best methods to measure the various forms of  $NO_x$ —NO,  $NO_2$ ,  $NO_Y$ , and speciated  $NO_Z$ . To accomplish this, scientific experts on monitoring methods were consulted, a program of in-house instrument testing and evaluation was initiated, and a literature search was undertaken. The instrument testing program included participation in the 1999 Nashville and Atlanta field studies that were organized under the Southern Oxidants Study (SOS) program. Scientists involved in diagnostic testing of current air quality models (AQMs) provided the performance criteria for candidate methods.

## Results and Implications

For the reactive oxides of nitrogen, the measurement criteria for diagnostic testing of models are no more than 20% uncertainty (10% for  $NO_2$ ) at concentrations of 1 ppbv and above, and a temporal resolution of significantly less than 1 hour. Current measurement methods for NO,  $NO_2$ ,  $NO_Y$ ,  $HNO_3$ , HONO, particle nitrate, and PAN and similar organic nitrates include methods that meet these criteria. However, these methods and their calibration procedures, with the exception of those for NO and  $NO_Y$ , are not widely used, or, in many cases, not generally available. For  $NO_2$  the most widely used method provides an upper limit to  $NO_2$  and does not meet the monitoring

criteria for diagnostic testing. Three other  $NO_2$  methods, photolytic conversion of  $NO_2$  to NO followed by  $NO/O_3$  chemiluminescence, UV differential optical absorption spectroscopy, and luminol chemiluminescence are commercialized. One or more of these three methods and/or the research method of laser induced fluorescence may be suitable for widespread use for diagnostic testing in the near term. For the other oxides of nitrogen, the lack of commercial incentives implies that diagnostic testing of AQMs prior to implementation of the  $NO_x$  SIP Call provisions (May 2004) will mostly involve specialized research methods.

Results of this report are directly relevant to the improvement of instrumentation for national monitoring networks including the Photochemical Assessment Monitoring Stations (PAMS), trends monitoring networks such as the Clean Air Status and Trends Network (CASTNET), and regulatory networks associated with the National Ambient Air Quality Standards.

#### Research Collaboration and Publications

The report describing this research was prepared as a collaborative effort of NERL staff and scientists at the National Oceanic and Atmospheric Administration Aeronomy Laboratory in Boulder, CO, the University of California (UC-LA, UC-Berkley, and UC-Riverside), and the on-site NERL contractor ManTech Environmental Technology, Inc. The report is entitled, "Recommended Methods for Ambient Air Monitoring of NO, NO<sub>2</sub>, NO<sub>y</sub>, and Individual NO<sub>z</sub> Species" and is identified currently as GPRA APM #442.

#### Future Research

Future research efforts to support the NO<sub>x</sub> SIP Call includes the improvement of commercial and research methods for NO<sub>2</sub>, HNO<sub>3</sub>, HONO, and particle nitrate monitors to meet monitoring criteria for diagnostic testing of AQMs. During 2001 and 2002, field testing of these instruments along with those for other species required in the diagnostic testing (including HCHO, H<sub>2</sub>O<sub>2</sub>, and speciated volatile organic compounds) are planned in cooperative efforts with NOAA and a number of public and private groups. This effort leads to a GPRA product in FY02 and supports the measurement of changes in ozone precursors before and after full implementation of the NO<sub>x</sub> State Implementation Plan Call provisions in May, 2004.

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